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# Development of laminated nickel/manganese oxide and nickel/niobium oxide electrochromic devices

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## ABSTRACT

We report on the preparation, electrical and optical analysis of electrodes and prototype electrochromic devices using a solid polymer ion conductor. For these devices we developed electrodes consisting of cobalt-doped nickel oxide, manganese-nickel oxide, and niobium oxide. Optical and voltammetric data was obtained for each electrode. Solid polymer electrolytes were synthesized from modified amorphous poly(ethylene oxide) [a-PEO] complexed with a metal silicate. Electrochromic devices were made using cobalt-doped nickel oxide/niobium oxide, and cobalt-doped nickel oxide/manganese-nickel electrode laminations. Optical spectra as a function of voltage was obtained for each device. Our best cobalt-doped nickel oxide/a-PEO/manganese-nickel oxide device showed photopic transmittance to be  $T_p(\text{bleached})=0.76$  and  $T_p(\text{colored})=0.44$ . The corresponding integrated solar transmittance was  $T_s(\text{bleached})=0.64$ ,  $T_s(\text{colored})=0.46$ . Our best cobalt-doped nickel oxide/a-PEO/niobium oxide device had photopic transmittance of  $T_p(\text{bleached})=0.65$  and  $T_p(\text{colored})=0.16$ . The corresponding integrated solar transmittance was  $T_s(\text{bleached})=0.45$  and  $T_s(\text{colored})=0.15$ . Of the two devices, the nickel/niobium oxide device had the best combination of electrical and optical properties. Better device properties are expected with improvements in the solid polymer electrolyte and lamination process.

## 1. INTRODUCTION

A number of electrochromic switching materials have been studied in the past few years.<sup>1</sup> For windows and other large-area applications, the most promising materials appear to be tungsten oxide, nickel oxide, and polyaniline.<sup>2,3</sup> One of the great challenges is to develop a solid-state device using nickel oxide. Recently, there has been an increase of interest in electrochromic nickel oxide for electrochromic switchable devices. In prior work, we have studied the switching characteristics and optical properties of nickel oxide in liquid electrolytes.<sup>4,5</sup> In other studies we have analyzed the chemistry of nickel oxide films by in-situ spectroscopic studies<sup>6</sup> and investigated their stability and durability.<sup>7</sup> Because liquid electrolytes are impractical for large-area devices, due to sealing and hydrostatic pressure considerations, we have concentrated on solid polymer ion conductors. In past work, we studied the properties of devices made with polymeric quaternary ammonium hydroxide, which switched nickel oxide well but had disadvantages of film etching and outgassing.<sup>8</sup> Since that time, we have developed a modified amorphous poly(ethylene oxide) [a-PEO] polymer ion conductors to serve as an ion transport media and as an adhesive lamination layer. We have modified a-PEO to be cast as a free standing film at room temperature and to retain its amorphous condition well below room temperature. By the addition of metal salts to the polymer we have been able to make lithium and proton/hydroxyl conducting polymer complexes.

In this work, our electrochromic devices consist of five layers: (1) transparent electronic conductor on glass, (2) electrochromic cobalt-nickel oxide, (3) polymer ion conductor, (4) metal oxide ion storage layer, and (5) transparent electronic conductor on glass. A schematic of our device design is shown in Fig. 1. Electrochromic devices will color or bleach when a potential difference of a few volts is applied between the working electrode and the counter-electrode. These devices exhibit good memory, maintaining a colored condition for several hours without external power. In the sections to follow, several electrochromic electrodes, are developed for devices. The electrodes are cobalt-doped nickel oxide, manganese-nickel oxide and niobium oxide. They are described by their voltammetry, current-voltage response, and transmittance properties.

## 2. EXPERIMENTAL PROCEDURES

A BAS potentiostat/coulometer (model CV-27) was used for deposition (except those sputtered) and analysis of the coatings. Cobalt-doped nickel oxide and manganese-nickel oxide films were deposited potentiostatically onto conductive indium-tin-oxide (ITO) coated glass electrodes (Donnelly Co, Holland, MI) using an appropriate sulfate deposition solution. The ITO electrodes were ultrasonically cleaned, dipped in ethyl alcohol, dipped in 10-20% sulfuric acid, rinsed in distilled water and dried in nitrogen. After deposition all electrodes were rinsed in distilled water and dried with nitrogen. The niobium oxide films were

deposited by either r.f. reactive sputtering or cathodic electrodeposition from a peroxide solution. In all electrode experiments the reference electrode was a Standard Calomel Electrode (SCE). Optical transmittance measurements were performed using a Cary 14 Spectrophotometer. In-situ spectrophotometry was performed using a special quartz cell with a micro-calomel reference electrode. The counter-electrode was a platinum sheet electrode. Both current and voltage were monitored during deposition. The electrodes were 3 x 5 cm in size. The active area as electrodes was 12.6 cm<sup>2</sup>. The active area was 3 x 3 cm or 9 cm<sup>2</sup> for devices.

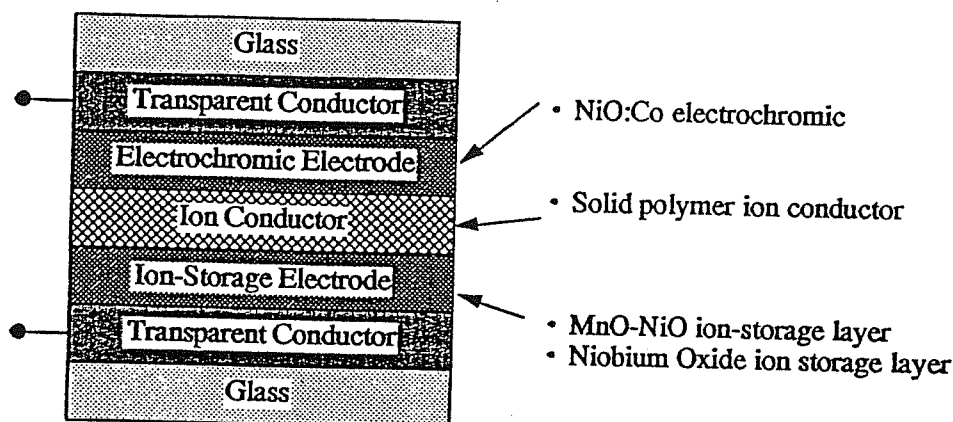


Fig. 1. Schematic of an electrochromic device showing the various layers and materials used (not to scale).

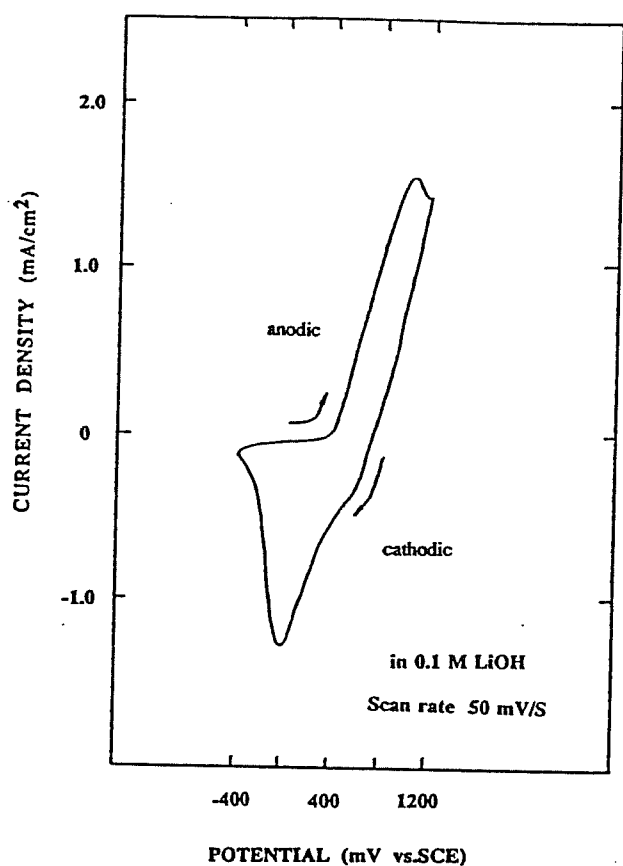
### 3. RESULTS AND DISCUSSION

#### 3.1. Cobalt-doped nickel oxide electrodes

It is known that cobalt additions to nickel oxide can increase stability and electrode utilization efficiency.<sup>9</sup> The current understanding of the effect on the structure of nickel oxide is that the cobalt ions occupy both the substitutional nickel sites and interlamellar sites. This was determined by Extended X-ray Absorption Fine Structure (EXAFS) studies.<sup>10</sup> Cobalt oxide and nickel oxide are very similar electrochemically.<sup>11</sup> The increase in oxygen overvoltage is beneficial to the stability of nickel oxide electrodes. Cobalt-doped nickel oxide films were deposited from a solution of 0.1M NiSO<sub>4</sub>·6H<sub>2</sub>O, 0.1M CoSO<sub>4</sub>·6H<sub>2</sub>O and 0.1M NH<sub>4</sub>OH. The films were made with a 2% cobalt sulfate-98% nickel sulfate concentration. The applied potential was a triangle potential from -200 mV to +1100 mV (SCE), with potential sweep rate of 50 mV/s. Typically, to deposit 120 nm (the thickness used for the electrodes in this study) of cobalt-doped nickel oxide 10 scans are needed.

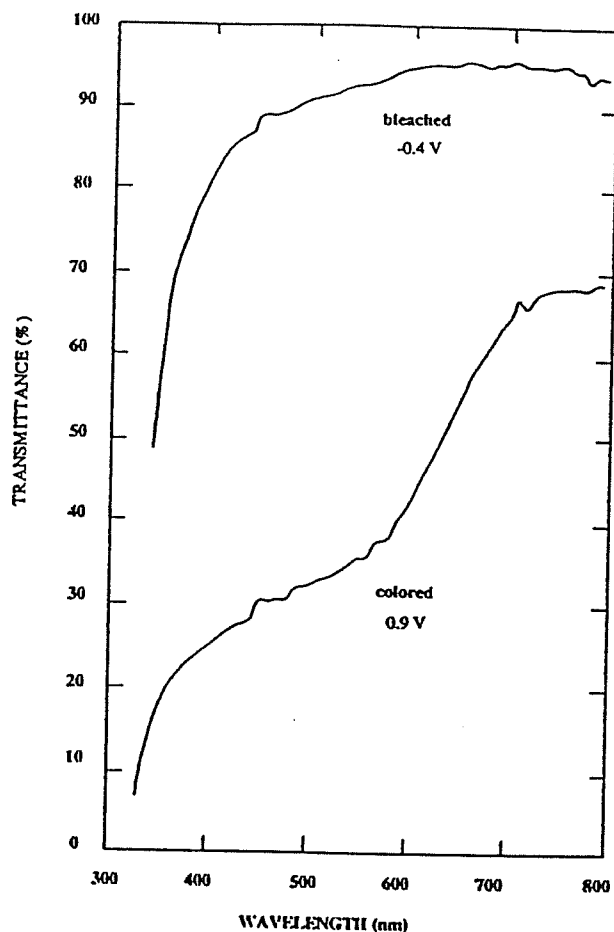
The voltammetry of the electrodes was acquired using a sawtooth potential ranging from -400 to 1200 mV at a scan rate of 50 mV/s. The results are shown in Fig. 2. During voltammetry measurements, it was possible to observe the switching of the electrode from the bleached (transparent), to the colored (brown-bronze) state. After the first few cycles, the voltammetry curves tend to exhibit reproducible behavior. In undoped nickel oxide, the oxygen gas evolution peak is near the anodic oxidation peak (coloration peak). Doping is used to increase the oxygen overvoltage. We cycled the electrodes in 0.1M LiOH to increase the oxygen overvoltage, compared to a KOH electrolyte.<sup>8,12,13</sup> The addition of lithium ions alters the chemical binding and electrostatic forces in the layered lattice of nickel hydroxide and increases the oxygen overvoltage by hindering the recombination of adsorbed oxygen.<sup>14</sup> The lithium ions help to tightly bind water in the interlayer structure of nickel hydroxide.<sup>15</sup> These factors provide the nickel hydroxide electrode with greater stability.

The visible transmittance of a nickel-cobalt oxide electrode is shown in Fig 3. Both the bleached and colored conditions are shown. The electrode was colored and bleached using static potentials of -0.4 and 0.9V. A broad optical absorption band is noted between 340 to 590 nm, with peak transmittance range of  $\Delta T_{550} = 0.57$ . The integrated photopic transmittance for the bleached to colored state is  $T_p = 0.93-0.39$ . The transmittance is about 10% higher than a comparable undoped nickel oxide electrode. The integrated (Air Mass 2) solar transmittance for this electrode is  $T_s = 0.68-0.37$  (data not shown in figure).



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Fig. 2. Cyclic voltammetry of electrochromic cobalt-doped nickel oxide electrode, cycled in 0.1 M LiOH at 50 mV/s.



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Fig. 3. Spectral transmittance of a cobalt-doped nickel oxide/ITO/glass electrode in 0.1M LiOH. (V vs SCE)

### 3.2. Manganese-nickel oxide electrodes

Manganese-nickel oxide films were investigated to serve as ion storage electrodes with high transparency and low coloration. Manganese-nickel oxide films were deposited onto ITO/glass electrodes from a solution of 0.1M  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and 0.1M  $\text{MnSO}_4 \cdot 6\text{H}_2\text{O}$  and 0.1M  $\text{NH}_4\text{OH}$ . We found that a range of stable manganese-nickel oxide films could be made from sulfate solutions. Pure manganese oxide films were found to be unstable, during cycling. Further information on manganese oxide can be found in our prior work<sup>16</sup>. For the data shown in Figs. 4 and 5, 60-80% manganese sulfate to 40-20% nickel sulfate concentrations were used to deposit films. The percentages refer to solution bath concentration relative to nickel sulfate, they do not refer to the chemical composition of the film. Both films were analyzed by XPS and found to have composition in rough correlation to the deposition concentration ratio. The 80% Mn-20% Ni sulfate films had composition in rough correlation to the deposition concentration ratio. The 80% Mn-20% Ni sulfate films had composition of 77.7% Mn and 22.3% Ni. The 60% Mn-40% Ni sulfate films had composition of 69.4% Mn and 30.6% Ni. The ratio of sulfate to ammonium ion concentration was kept constant. A triangle potential was used for deposition with values of -400 mV to +900 mV (SCE) with sweep rate of 50 mV/s.

For voltammetry and optical transmittance measurements, the electrodes were cycled in 0.1M LiOH using a calomel electrode and platinum counter-electrode. A voltage range of -400 to 900 mV at a scan rate of 50 mV/s was used. The cyclic voltammetry for several manganese-nickel electrodes is shown in Fig. 4. The addition of manganese beneficially increased the oxygen overvoltage. From 20-60% manganese concentrations, the charge capacity of the electrode is acceptable for devices. In this study all electrodes used for devices were 60% manganese-40% nickel oxide. The 80% manganese oxide electrode is stable but the charge capacity of the electrode is low. The optical transmittance of nickel oxide and manganese-nickel oxide electrodes

are shown in Fig. 5 Both the bleached and colored conditions are shown. The 60% manganese oxide electrode has a peak absorption at 390 nm with transmittance change of  $\Delta T_{\text{peak}} = 0.26$ . The photopic transmittance is  $T_p = 0.80-0.60$ , with corresponding solar transmittance of  $T_s = 0.54-0.47$  (data not shown). The shape of the absorption curve signifies a change in color compared to nickel. The manganese-nickel films are golden-yellow in color.

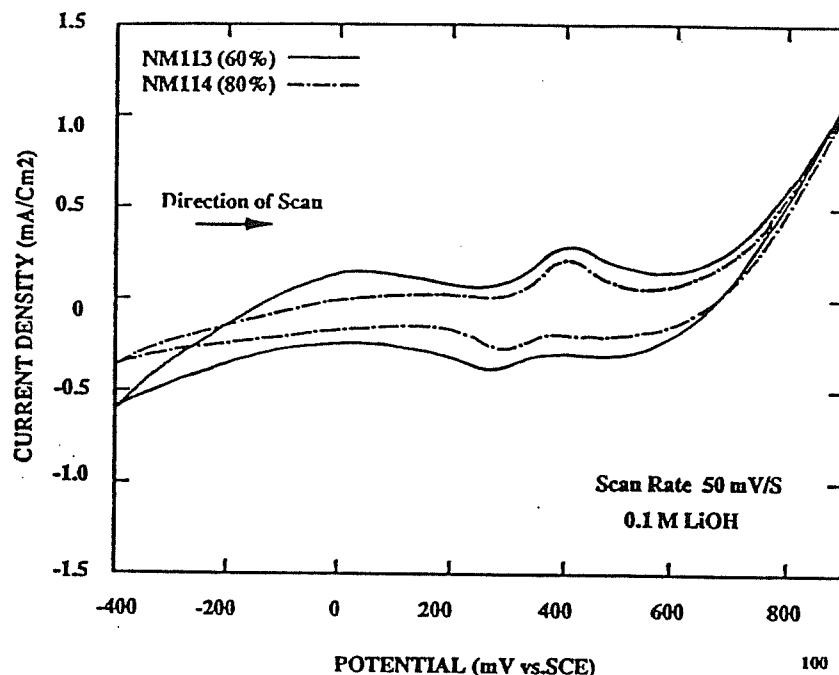


Fig. 4. Cyclic voltammetry of electrochromic manganese-nickel oxide/ITO/glass electrodes, cycled in 0.1 M LiOH at 50 mV/s. Shown is data for 60% manganese-40% nickel oxide and 80% manganese-20% nickel oxide electrodes.

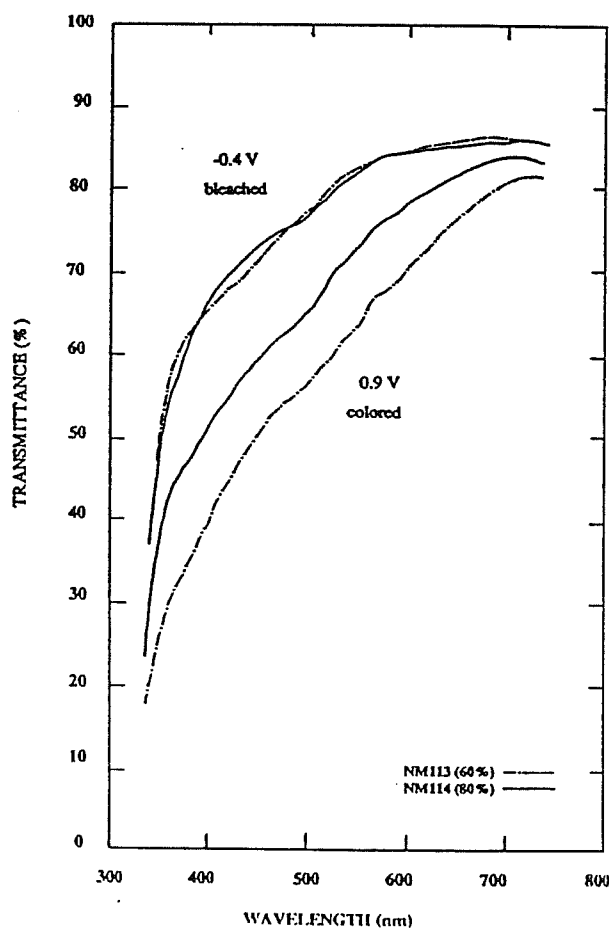


Fig. 5. Optical transmittance of electrochromic manganese-nickel oxide ITO/glass electrodes. Curves are shown for the colored and bleached conditions for 60 and 80% manganese-nickel electrodes. They are cycled in 0.1 M LiOH.

### 3.3. Niobium oxide electrodes

Niobium films were deposited for use as complementary electrochromic electrodes for nickel oxide devices. Niobium oxide is known as a storage electrode material for lithium<sup>17-20</sup> and protons.<sup>21-23</sup> It colors from transparent to blue in acid media. In alkaline LiOH we found that it colored to a grey. Niobium oxide sputtered films were deposited with 100 W of r.f. power (13.6 MHz) from a 12 cm diameter niobium target (Cerac, Corp.) with a reactive gas mixture of 13 mT Argon+2 mT Oxygen and a substrate temperature of 200 C. The target to substrate distance was between 5.5-7.0 cm. The film thickness was about 250 nm<sup>17</sup>. Also, we deposited niobium oxide films were deposited electrochemically from a solution of niobium metal dissolved in 30% H<sub>2</sub>O<sub>2</sub>. Due to the low reactivity of niobium it was difficult to deposit. Niobium films were deposited onto ITO electrodes using a triangle potential of -700 to -200 mV (SCE) at 50 mV/s. After the films were deposited they were rinsed in distilled water and dried with nitrogen

For voltammetry, and optical transmittance measurements, the electrodes were cycled in 0.1M H<sub>2</sub>SO<sub>4</sub> and 0.1M LiOH using a calomel reference electrode and platinum counter-electrode. Cyclic voltammetry for the film is shown in Fig. 6. A voltage range of -2400 to 2000 mV (SCE) and a scan rate of 50 mV/s were used. In both electrolytes, the film colors at negative potentials. The sharp negative peak is part of the hydrogen evolution peak.

Normal transmittance measurements on a niobium oxide electrode were made over the visible wavelength regions. The electrode was colored using static potentials of 1.5 and -2.0V (SCE) in 0.1M LiOH. Similar results were obtained for 0.1M H<sub>2</sub>SO<sub>4</sub>. In sulfuric acid we noticed etching of the electrode, especially at the electrolyte-air interface. The typical spectral transmittance of a niobium oxide electrode in a cell is shown in Fig.7. The photopic transmittance of the niobium oxide electrodes in an electrochemical cell is  $T_p = 0.76$  bleached and when colored (-2.0V) switches to  $T_p = 0.24$ . During cycling we have found these films to be very stable.

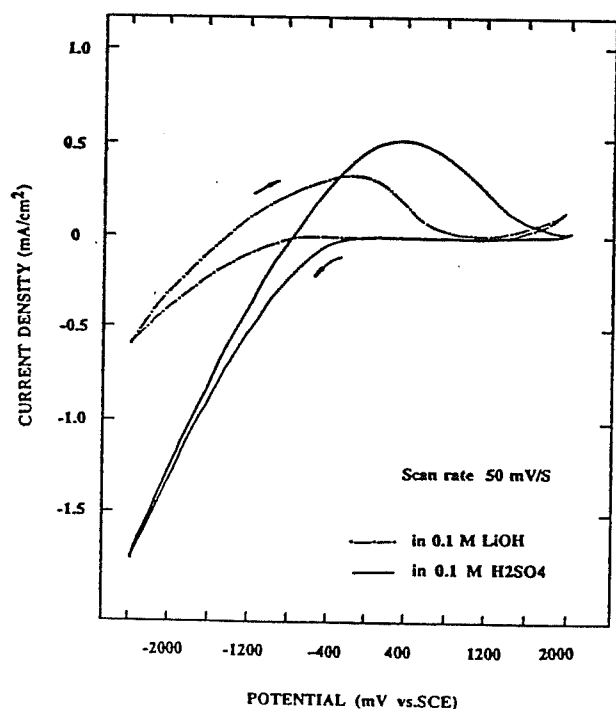


Fig. 6. Voltammetry for a niobium oxide ITO/glass electrode in 0.1 M H<sub>2</sub>SO<sub>4</sub> and 0.1 LiOH electrolytes. The scan rate is 50 mV/s.

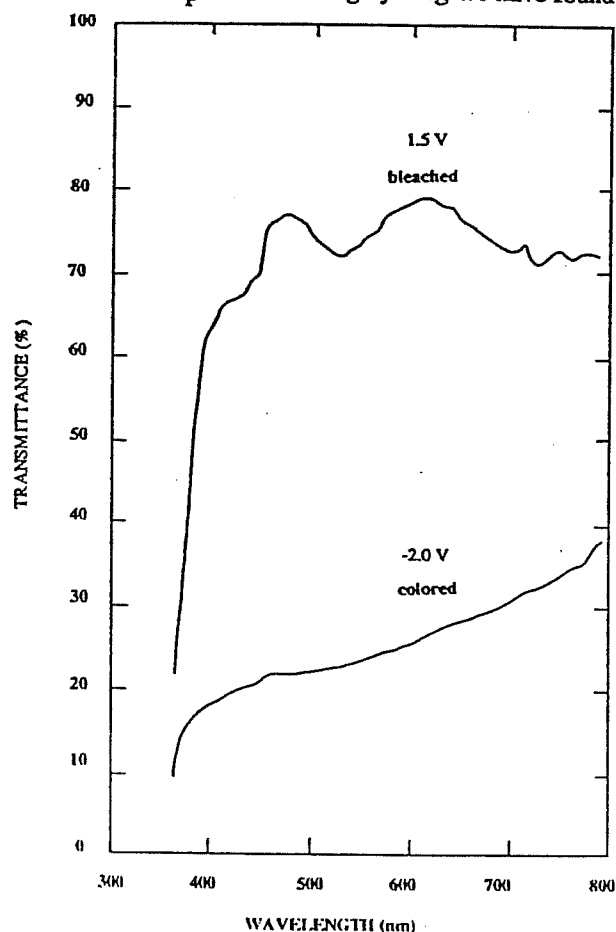


Fig. 7. Normal transmittance for electrochromic niobium oxide ITO/glass electrode in a liquid cell with 0.1M LiOH electrolyte. Transmittance is shown for colored and bleached conditions (V vs SCE).

### 3.4. Solid polymer electrolytes

The polymer ion conductor used for devices is based on modified a-PEO. This polymer was chosen for a variety of reasons. It has been used very successfully in polymeric batteries and a-PEO has one of the highest ionic conductivities known for a polymer.<sup>24</sup> Also, it is a fairly simple linear polymer, with reasonable solubilities in a variety of solvents and salts. Amorphous PEO is highly transparent (greater than 95% in the visible region) and with certain modifications can be formed into free standing films or be used for solution and spin coating. These coatings are highly elastic and adhesive so they can serve as a laminating polymer for devices and can withstand temperatures to 170 C. Finally, they are low cost, non-toxic in their final form. This polymer is used as the base material for the ion conductor and can be modified for different ions and devices.

High molecular weight a-PEO in a suitable solvent is used as a base for the ion conductor. Solutions of about 2-4% weight PEO to solvent were made. To this is added a salt, such as lithium triflate ( $\text{LiCF}_3\text{SO}_3$ ) and a metal silicate to enhance anion or hydroxyl conduction. In general, the addition of soluble salts and oxides did not greatly alter the optical properties of the a-PEO film. A 5  $\mu\text{m}$  thick film of PEO has about 95% transmission from 300 to 1100 nm. These polymers are coated on electrodes using solution casting.

### 3.5 Device fabrication and analysis

The electrochromic device is constructed from two coated electrodes. Lamination is performed in air after drying of the ion conductor layer. The edges of the device were sealed with a hot melt adhesive. Care must be taken to insure that the sealant and its curing byproducts do not react with or interfere with the polymer or electrochromic layers. Reference electrodes were not used in these fabrications. Completed 3 x 3 cm devices were tested using a custom d.c power supply with current regulation. All voltages are relative to the nickel oxide electrode. The devices were optically evaluated in-situ, using a spectrophotometer. The spectra of three representative devices are shown in Figs. 8-11 and 13. Spectral visible data is shown in Figs. 8 and 9 and solar data is shown in Figs. 10 and 11. Optical data on all devices is in Table 1. The transmittance in Figs. 8 and 10 is for a nickel oxide:Co/a-PEO/manganese-nickel oxide device. This device colored well, between 1.4 to 2.0V. This device switched from  $T_p(\text{bleached})=0.76$  to  $T_p(\text{colored})=0.44$ . The corresponding integrated solar transmittance was  $T_s(\text{bleached})=0.64$  and  $T_s(\text{colored})=0.46$ . The transmittance of a nickel oxide:Co/a-PEO/ niobium oxide device is shown in Figs 9 and 11. This device uses the complementary design consisting of anodic (nickel oxide) and cathodic (niobium oxide) coloring electrochromics. In this design, both electrodes color together to a grey-bronze. Both electrodes color but not as strongly as they do independently of each other. This device switched from  $T_p(\text{bleached})= 0.65$  to  $T_p(\text{colored})=0.16$ . The corresponding solar transmittance was  $T_s(\text{bleached})=0.45$  and  $T_s(\text{colored})=0.15$ . The switching voltages were -0.7 and 1.9V (relative to the nickel electrode) The current-Voltage characteristics for this device are shown in Fig. 12.

The transmittance of another nickel oxide:Co/a-PEO/ niobium oxide is shown in Fig. 13. This device had both oxide layers deposited electrochemically. In this case the niobium oxide layer is about a third the thickness of the sputtered film (under 100 nm) This device switched from  $T_p(\text{bleached})= 0.57$  to  $T_p(\text{colored})=0.20$ . The corresponding solar transmittance was  $T_s(\text{bleached})=0.44$  and  $T_s(\text{colored})=0.22$ . The switching voltages were -1.0 and 1.5V (relative to the nickel electrode). With improved electrochemical deposition methods for niobium oxide it is expected that this device could equal that of one with the sputtered film.

Table 1. Nickel-oxide/a-PEO/metal oxide devices

Device	Peak $\lambda$ , nm	$\Delta T_{\text{peak}}$	$T_p(\text{B-C})$	$T_s(\text{B-C})$
NiO:Co/a-PEO+Silicate/MnO-NiO	590	37	76-44	64-46
NiO:Co/a-PEO+Silicate/Nb <sub>2</sub> O <sub>5</sub>	590	53	65-16	45-15
NiO:Co/a-PEO+Silicate/Nb <sub>2</sub> O <sub>5</sub>	550	39	57-20	44-22

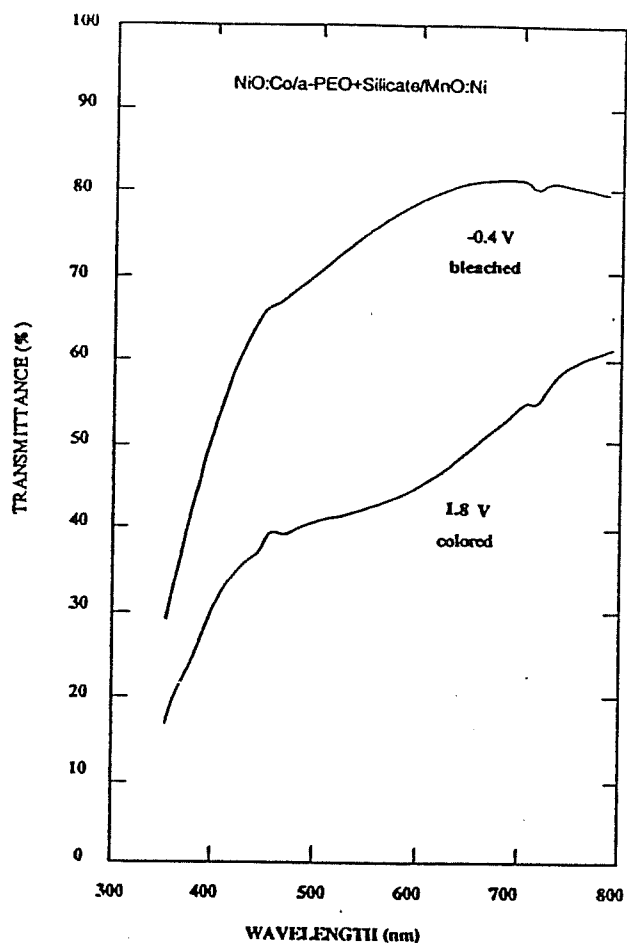


Fig. 8. Optical transmittance of electrochromic nickel oxide/a-PEO/ manganese-nickel oxide device.

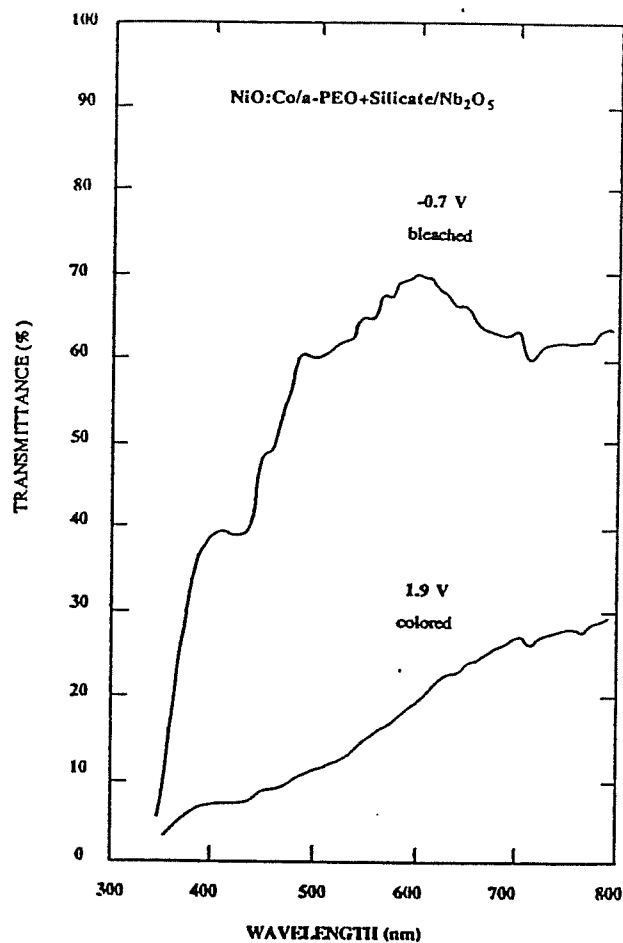


Fig. 9. Optical transmittance of electrochromic nickel oxide/a-PEO/niobium oxide device.

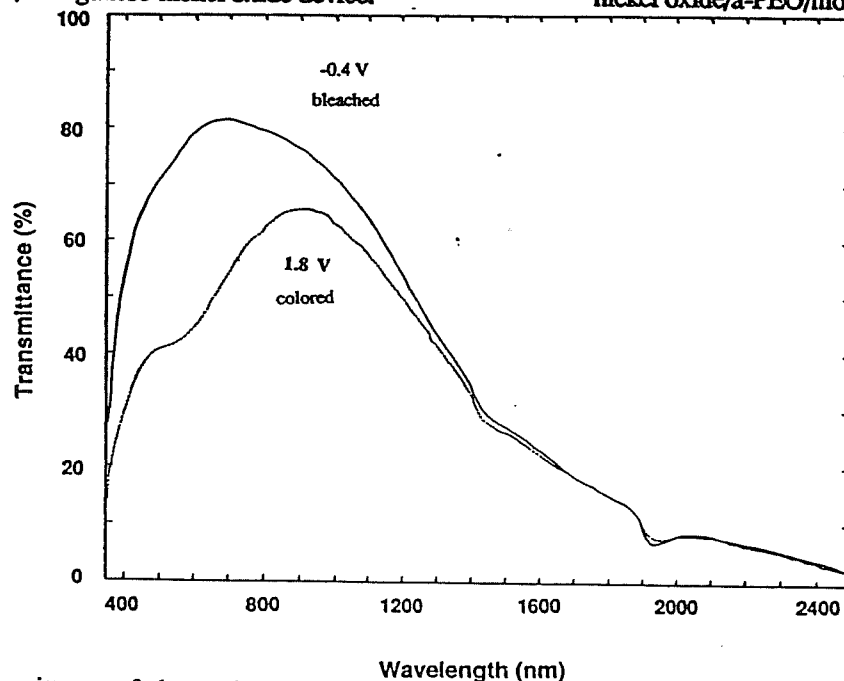
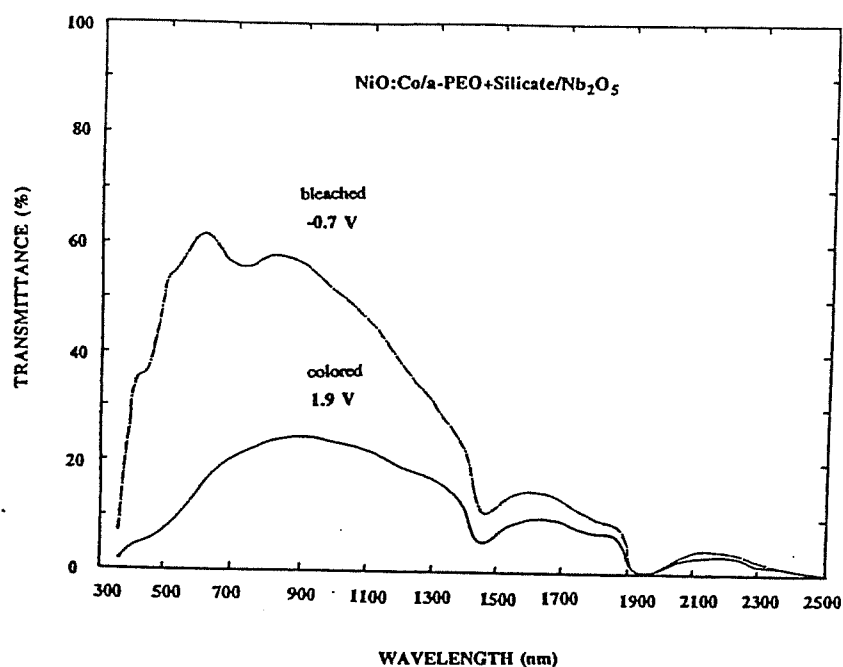


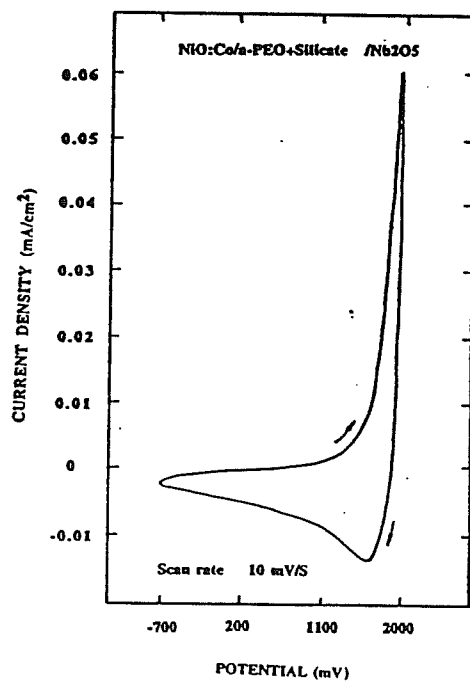
Fig. 10. Solar Transmittance of electrochromic nickel oxide:Co/a-PEO/ manganese-nickel oxide device (shown in Fig 8).





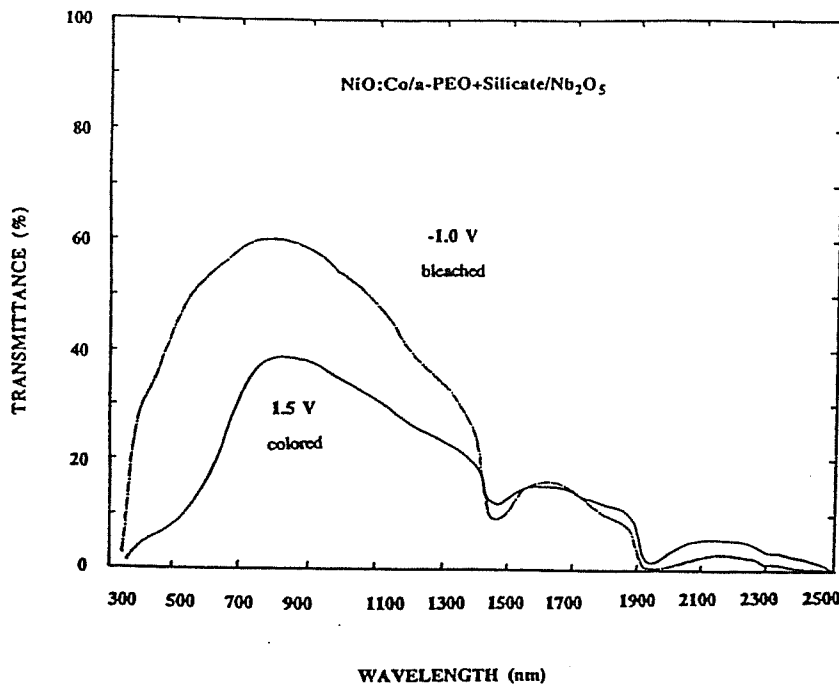
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Fig. 11. Solar Transmittance of electrochromic nickel oxide:Co/a-PEO/ niobium oxide device (shown in Fig. 9).



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Fig. 12. Current-Voltage characteristics for the nickel oxide:Co/a-PEO/ niobium oxide device in Figs. 9 and 11.



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Fig. 13. Solar Transmittance of electrochromic nickel oxide:Co/a-PEO/ niobium oxide device. Both oxide layers were deposited electrochemically.

#### 4. CONCLUSIONS

Our work on electrodes has shown that excellent electrochromic electrodes can be made for nickel oxide devices. The basic nickel oxide electrode can be improved by 2% doping with cobalt, resulting in an electrode with  $T_p$  range of 0.93-0.39. Small amounts of cobalt increase the switching range of nickel oxide while increasing the oxygen overvoltage. By the addition of 50% or greater manganese to nickel oxide, the electrodes decrease their switching but retain their charge storage characteristics. We obtained a photopic transmittance range of  $T_p = 0.80-0.60$  for a 60% manganese-nickel oxide electrode. This electrode was used as a counter-electrode for cobalt-doped nickel oxide devices. High quality niobium oxide films have been successfully deposited by reactive sputtering and from a metal peroxide solution. The sputtered film had a photopic transmittance range of  $T_p = 0.76-0.24$  for 250 nm film thickness.

Our best nickel oxide:Co/a-PEO/manganese-nickel device showed the photopic transmittance to be  $T_p(\text{bleached})=0.76$  and  $T_p(\text{colored})=0.44$ . The corresponding integrated solar transmittance was  $T_s(\text{bleached})=0.64$  and  $T_s(\text{colored})=0.46$ . Our best nickel oxide/a-PEO/niobium device showed the photopic transmittance to be  $T_p(\text{bleached})=0.65$  and  $T_p(\text{colored})=0.16$ . The corresponding integrated solar transmittance was  $T_s(\text{bleached})=0.45$  and  $T_s(\text{colored})=0.15$ . The nickel:Co oxide/a-PEO/niobium oxide device, using the sputtered niobium oxide film, had the best overall characteristics of all the devices. With further improvements in the a-PEO ion conductor and lamination we expect to see even better optical values for this class of device.

#### 5. ACKNOWLEDGMENTS

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